# Atmospheric Deposition of Nutrient Nitrogen to Galveston Bay, Texas

**Stephen T. Sweet**

Geochemical and Environmental Research Group
College of Geosciences
Texas A&M University
833 Graham Road
College Station, Texas 77845
(409) 862-2323 EXT 133
(409) 862-2361 FAX
sweet@gerg.tamu.edu

## EDUCATION:

M.S. Texas A&M University, 1988 (Chemical Oceanography)
B.S. McGill University, 1980 (Marine Science)

## EXPERIENCE:

| | |
|---|---|
| 1989- Present | Research Associate, Geochemical and Environmental Research Group, College of Geosciences, Texas A&M University. |
| 1984-1989 | Research Assistant, Geochemical and Environmental Research Group, College of Geosciences, Texas A&M University. |
| 1981-1984 | Graduate Assistant Research, Department of Oceanography, Texas A&M University. |
| 1980-1981 | Graduate Assistant Teaching, Department of Mathmatics and Department of Biology, Texas A&M University. |

# ATMOSPHERIC DEPOSITION OF NUTRIENT NITROGEN TO GALVESTON BAY, TX

Stephen Sweet
Terry L. Wade
Junesoo Park
David Wylie
Geochemical and Environmental Research Group
Texas A&M University
833 Graham Road
College Station, TX. 77845
Luis Cifuentes
Department of Oceanography
Texas A&M University
College Station, TX 77843

Nitrogen compounds can have both beneficial (e.g., soil fertility, plant nutrient) and harmful effects (ozone destruction, greenhouse effect, air pollution, acid rain, acidification and eutrophication of surface waters, and contamination of ground water). EPA considered these deleterious effects and has a mandate to evaluate and regulate nitrogen compounds under the Clean Air Act, the Clean Water Act, the Drinking Water Act, etc. Beside agricultural and sewage loadings of nitrogen via river and direct discharge, deposition of atmospheric nitrogen may be a major fraction of anthropogenic nitrogen loadings to coastal ecosystems, which may cause harmful eutrophication. In order to fulfill the mandates of the Great Waters Program and the Clean Air Act Amendments of 1990 (112 m), the US EPA initiated monitoring research in important and representative water bodies, including coastal waters. As part of this program the Texas Regional Integrated Atmospheric Deposition Study (TRIADS) was established with a sampling site located in Seabrook, Texas (see Figure 1) in order to monitor atmospheric deposition of contaminants to Galveston Bay. Wet depositional nutrient monitoring at the TRIADS site started on February 2, 1995 and was in continuous operation until August 6, 1996.

The concentrations of atmospheric nitrate and ammonium depend on the amount of precipitation (Liken et al, 1987) and on the character of the air mass (Shon, 1994). Nitrate and ammonium appear to be derived primarily from gaseous constituents of the atmosphere (Gambell and Fisher, 1964). Different air masses reaching the sampling site appeared to cause temporal variations in both inorganic and organic nitrogen concentrations in the precipitation (Loye-Pilot et al., 1990; Shon, 1994). The natural sources of nitrate in rain are lightning, causing the formation of nitric oxide, photochemical oxidation in the stratosphere of $N_2O$ to NO and $NO_2$, chemical oxidation

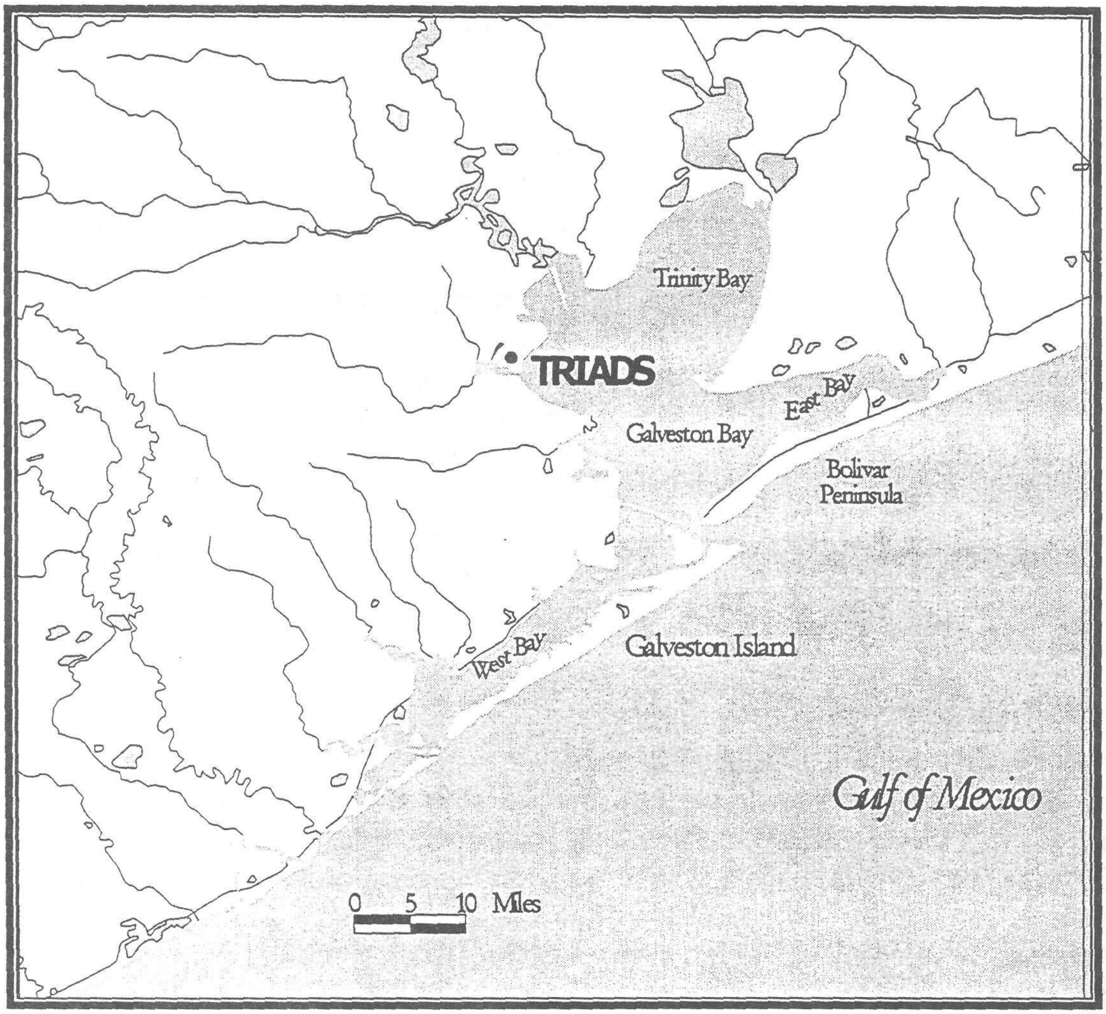


Figure 1. TRIADS Site Location Seabrook, Texas.

in the atmosphere of ammonia to $No_x$, and soil production of NO by microbial processes. The anthropogenic sources of nitrate in rain are fossil fuel burning, primarily in automobile engines, power plants, and biomass burning (Logan, 1981). Ammonia is found as gaseous $NH_3$ and $NH_4^+$ in aerosol formed in the atmosphere. Ammonium results from the reaction of ammonia gas (NH3) with water ($NH_3 + H_2O \rightarrow NH_4^+ + OH^-$). Thus, the presence of gaseous ammonia in the atmosphere has been inferred by the measurement of the NH4+ ion in rainwater (Junge, 1963, McConnel, 1973). Atmospheric ammonia is produced mainly by the decay of animal and human excrements, bacterial decomposition of natural nitrogenous organic material in natural soils, the volatilization from nitrogen fertilizer, and combustion of coal (Shon, 1994). Urea is likely to be directly volatilized from land and water surfaces into the atmosphere (Healy et al., 1970). Urea as a high percentage of the total dissolved organic nitrogen (DON) concentrations have been reported in New Zealand, Japan (Timperley et al., 1985), and Texas (Shon, 1994).

The nutrient concentrations in µmol/L determined for the TRIADS study in rain samples collected between February 25, 1995 and August 6, 1996 are reported in Table 1. Total nitrogen is the sum of $NH_4$, Urea, $NO_3$, and $NO_2$. The predominant nitrogen species is either $NO_3$ or occasionally $NH_4$. The concentrations for $PO_4$ and $SiO_3$ were low and do

Table 1. TRIADS Nutrient and Rainfall Data

| Collection Period | Days | Number of Rain Events | Rain (mm) | $NH_4$ | UREA | $NO_3$ | $NO_2$ | TOTAL N |
|---|---|---|---|---|---|---|---|---|
| 54-69 | 15 | | 103.3 | 11.14 | 0.39 | 17.41 | 0.03 | 28.97 |
| 69-74 | 5 | 2 | 43.0 | 5.47 | 0.44 | 4.71 | 0.03 | 10.65 |
| 74-97 | 23 | 1 | 18.5 | 10.25 | 0.73 | 4.11 | 0.04 | 15.13 |
| 97-129 | 32 | 2 | 44.2 | 24.61 | 1.08 | 41.70 | 0.19 | 67.58 |
| 129-147 | 28 | 1 | 9.6 | 28.93 | 1.92 | 32.81 | 1.06 | 64.72 |
| 147-159 | 12 | 5 | 200.1 | 17.72 | 0.70 | 5.60 | 0.18 | 24.20 |
| 159-181 | 22 | 6 | 92.6 | 7.41 | 0.34 | 357.35 | 0.02 | 365.12 |
| 181-204 | 23 | 5 | 84.7 | 8.90 | 0.35 | 17.08 | 0.03 | 26.36 |
| 204-214 | 10 | 3 | 44.8 | 6.10 | 0.34 | 27.85 | 0.03 | 34.32 |
| 214-235 | 21 | 1 | 1.2 | 5.37 | 0.48 | 64.10 | 0.03 | 69.98 |
| 235-265 | 20 | 9 | 61.2 | 2.24 | 0.22 | 17.63 | 0.03 | 20.12 |
| 265-282 | 17 | 4 | 21.3 | 6.14 | 0.30 | 45.50 | 0.04 | 51.98 |
| 282-304 | 22 | 3 | 23.7 | 4.64 | 0.26 | 38.03 | 0.03 | 42.96 |
| 304-326 | 22 | 3 | 171.6 | 6.58 | 0.30 | 3.84 | 0.06 | 10.78 |
| 326-353 | 27 | 2 | 140.2 | 5.02 | 0.29 | 8.40 | 0.04 | 13.75 |
| 353-14 | 26 | 3 | 50.6 | 3.30 | 0.15 | 14.33 | 0.03 | 17.81 |
| 14-56 | 42 | 2 | 79.8 | 3.16 | 0.51 | 21.40 | 0.03 | 25.10 |
| 56-75 | 19 | 2 | 15.8 | 0.11 | 0.24 | 7.35 | 0.02 | 7.72 |
| 75-154 | 79 | 3 | 86.7 | 15.29 | 0.46 | 18.58 | 0.02 | 34.35 |
| 154-219 | 65 | 6 | 89.9 | 0.12 | 0.22 | 10.32 | 0.02 | 10.68 |

not have a simple relationship to total nitrogen. The ratio of total nitrogen to $PO_4$ is over 100 indicating that contamination of rain samples from bird feces was minimal. The $PO_4$ concentrations were low and ranged from 0.02 to 0.22 µmol/L. The $SiO_3$ concentrations were also low and ranged from 0.01 to 0.25 µmol/L. By comparison, total nitrogen concentrations ranged from 7.72 to 365 µmol/L. The highest concentration was present predominantly as $NO_3$ (357 µmol/L) and this concentration was confirmed by separate analyses of the trace element sample for $NO_3$ (385 µmol/L). The second highest total nitrogen concentrations was 70 μmol/L. There is no apparent correlation between rainfall amount and nutrient nitrogen concentration.

Meteorological data logged at the TRIADS station can help explain the variability in the wet deposition of nitrogen at the Seabrook site. Figures 2 and 3 show the wind speed and direction for the two rain events that were collected during the sampling period with the highest total nitrogen. Figure 4 shows the precipitation data (mm) for the same sampling period. During the first rain event on June 11, 1995, 32.5 mm of rain accumulated. Due to forcing caused by a synoptic front, the wind direction shifted from southeasterly to throughout the event. These conditions provided air over the sampling site that was advected from the heavily industrialized Houston area northwest of the sampling site. This advected air could be the source of the nitrogen. The dissipation of nitrogen while enroute was minimized due to decreased winds and the subsidence caused by the high pressure that followed the front. Subsidence over the Houston area would inhibit upward mixing of the lower atmosphere maintaining high nitrogen concentrations as the air moved over the Seabrook site. The second rain event deposited roughly twice as much rain, 60 mm from June 29, 1995 to June 30, 1995. The day of sample collection immediately followed this rain event. The wind direction was predominantly from the northeast-easterly quadrant during the precipitation event. These conditions provided air over the sampling site that was advected from an industrialized zone east of the Houston area.

In contrast, meteorological data collected during periods of relatively low total nitrogen deposition, the wind direction was predominantly from the southeasterly quadrant. Figures 5 and 6 show data wind speed and direction, and precipitation data collected during the collection period from 147 to 159 where the total nitrogen wet deposition was relatively low (24.2 μmol/L). These conditions provided air over the sampling site that was advected from the Gulf of Mexico.

A linear relationship, with a correlation coefficient ($r^2$) of 0.956, between cumulative rainfall and Julian day was observed for the sampling period from February 2, 1995 through August 6, 1996. The average rainfall during this study was 963 mm/year, approximately 25% below the average rainfall to Galveston Bay of approximately 1270 mm/ year. Cumulative nutrient nitrogen deposition in Kg N/hectare versus Julian Day is plotted in Figure 7. The plot would provide a linear line fit, except for the large rain nitrogen deposition between the two sampling periods from 147 to 159 and 159 to 181. The yearly nitrogen deposition rate to Galveston Bay was 6.16 Kg/hectare-year. This number can be used in the model by Patwardhan and Donigian (1995) to provide an estimate of the nitrogen budget for Galveston Bay. This model assumes that wet deposition is equal to dry deposition so total deposition would be 12.2 kg/ hectare-year. The total input from atmospheric deposition of nutrient nitrogen directly to the Bay is estimated as $1.76 \times 10^6$ Kg/year or 8.6% of the total nutrient nitrogen input to Galveston Bay with another 2.8% from atmospheric input to the watershed. Therefore, atmospheric inputs supplies about 10% of the nutrient nitrogen to Galveston

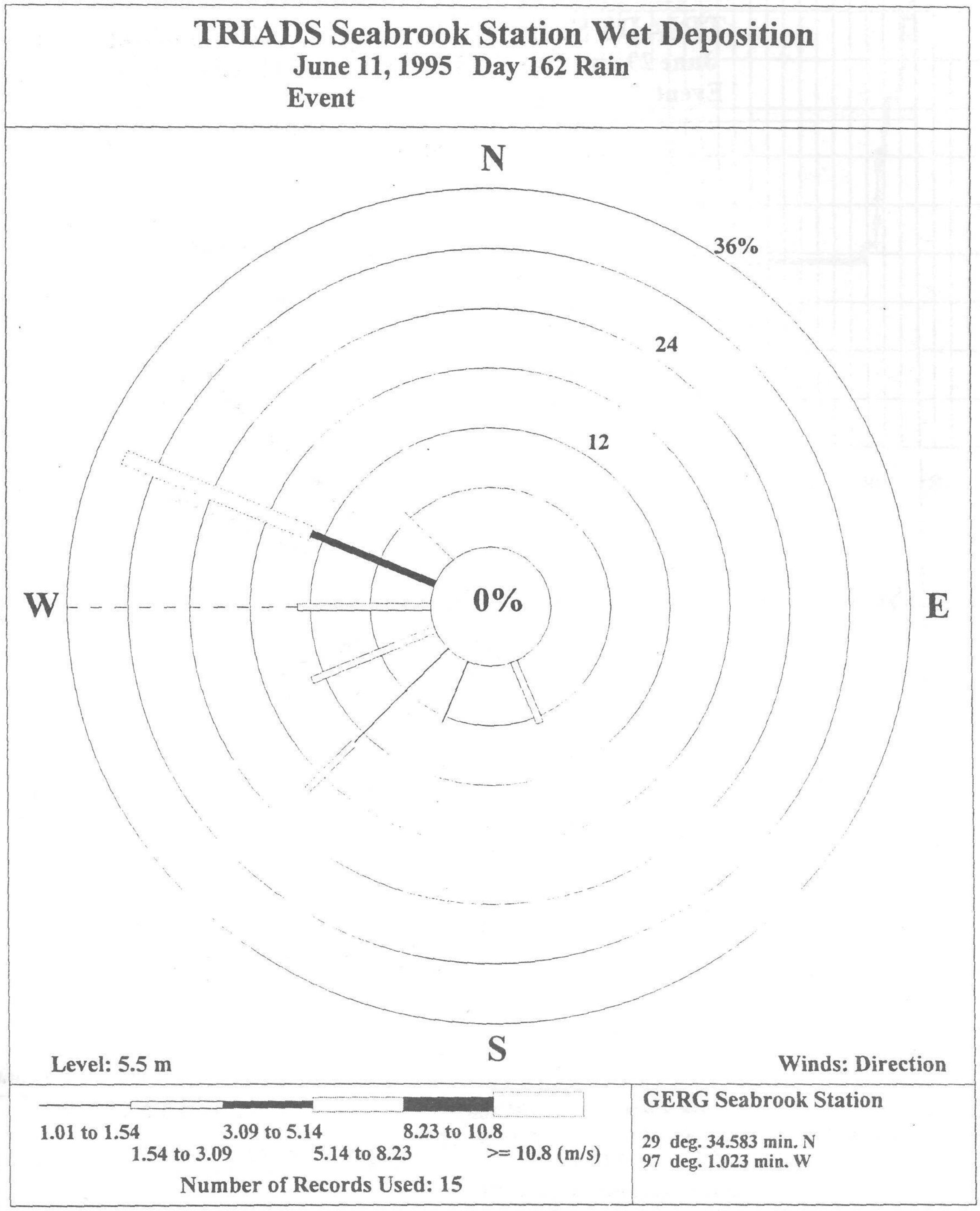


Figure 2. Wind Speed and Direction During June 11, 1995 Rain Event.

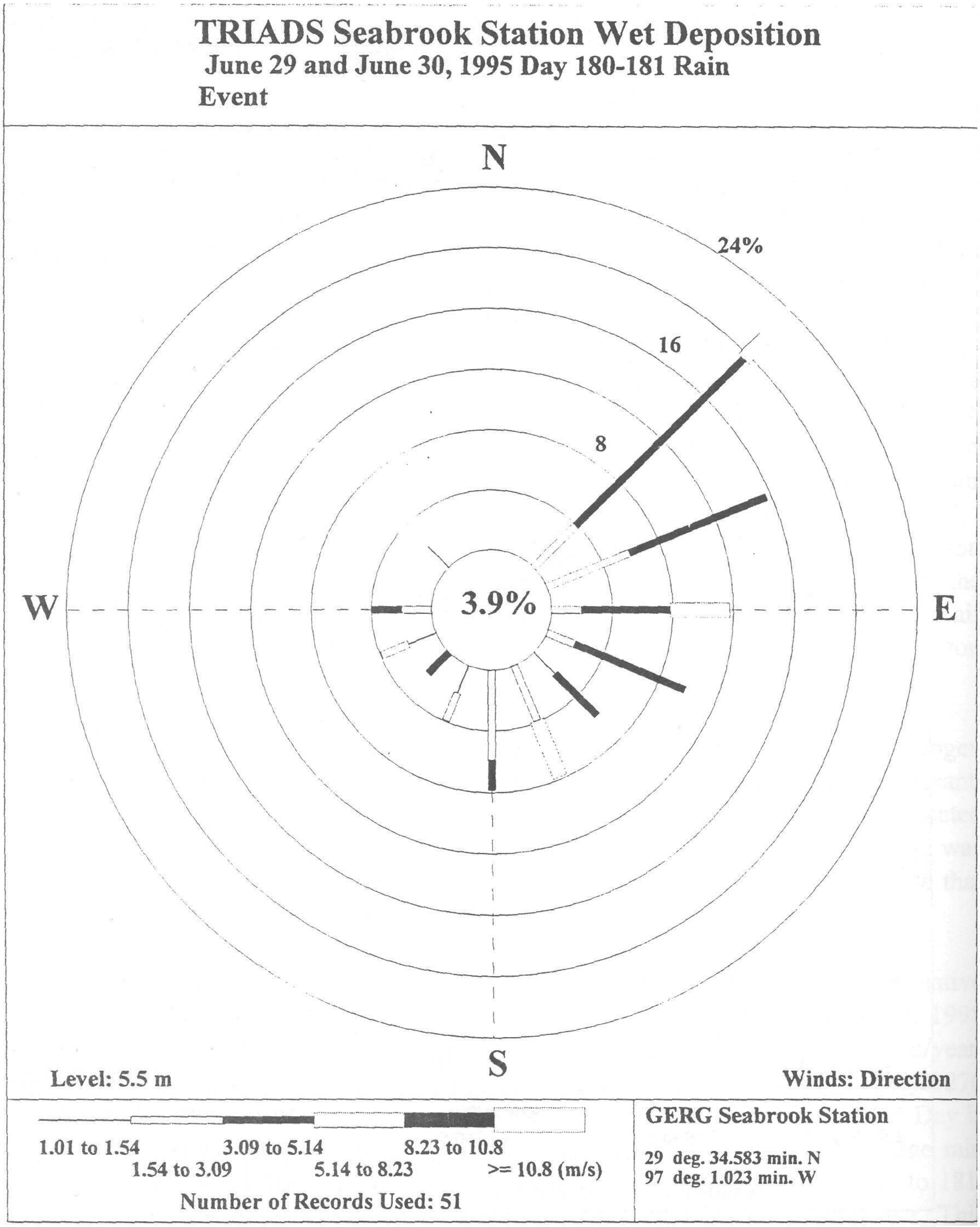


Figure 3. Wind Speed and Direction During June 29&30, 1995 Rain Event.

June 8, 1995 through June 30, 1995 Seabrook Station

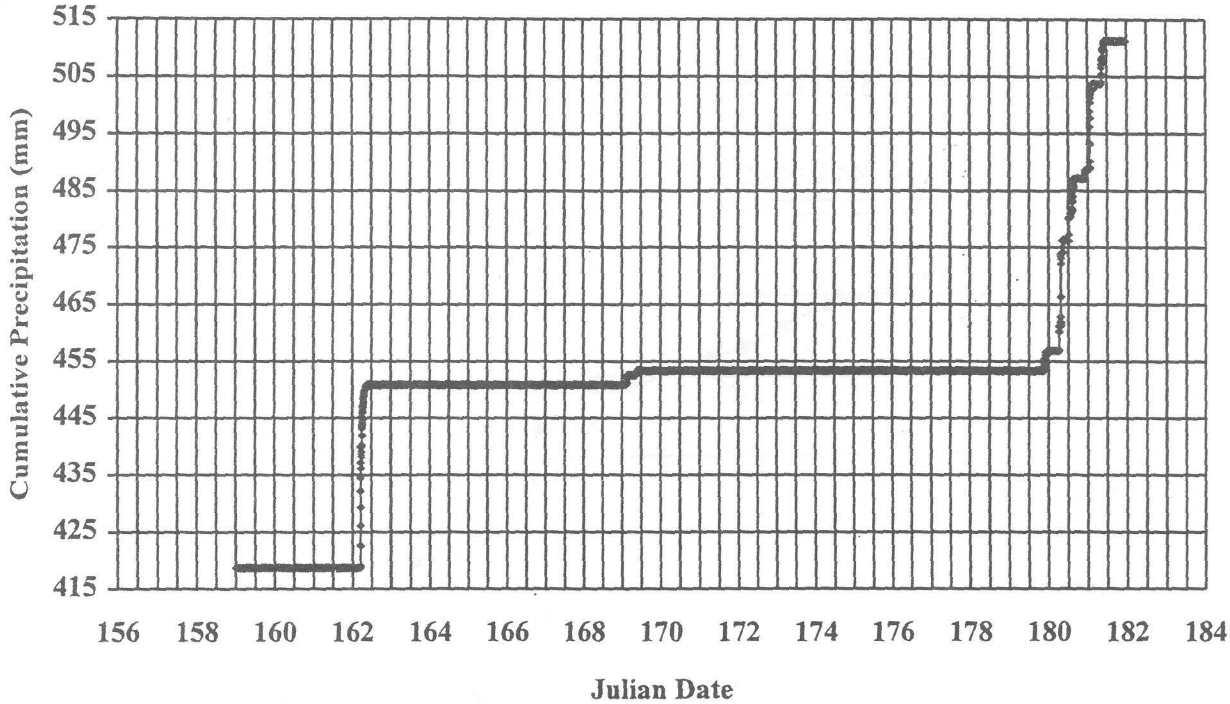


Figure 4. Cumulative Precipitation (mm) During Sampling Period 159-181

May 27, 1995 through June 8, 1995 Seabrook Station

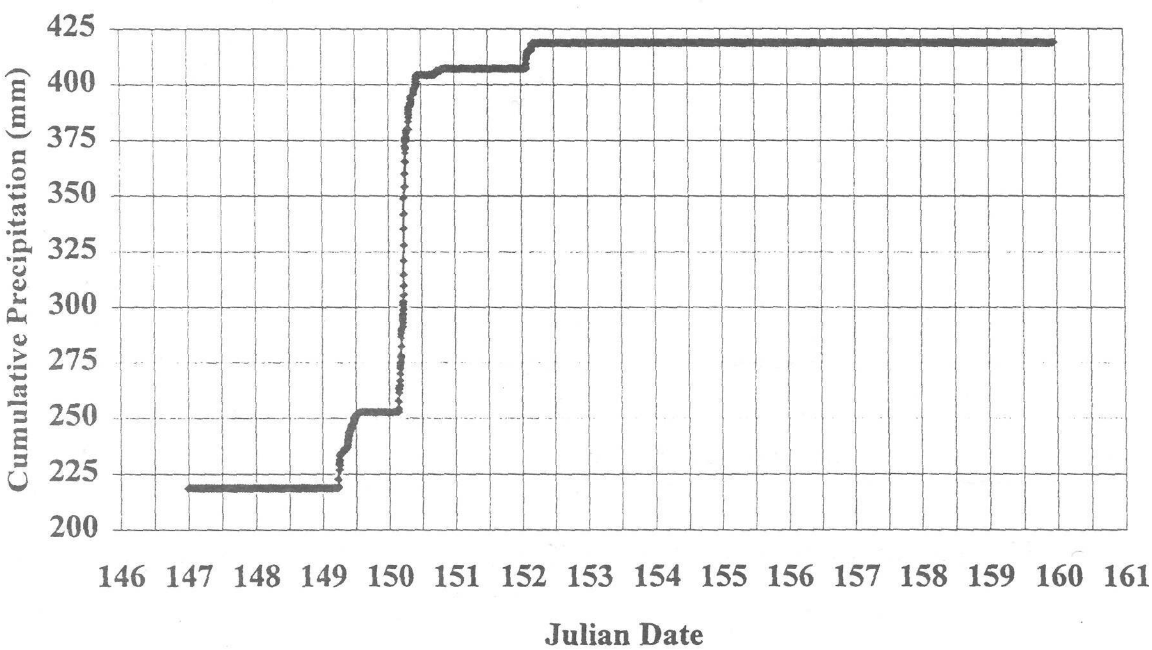


Figure 5. Cumulative Precipitation (mm) During Sampling Period 147-159.

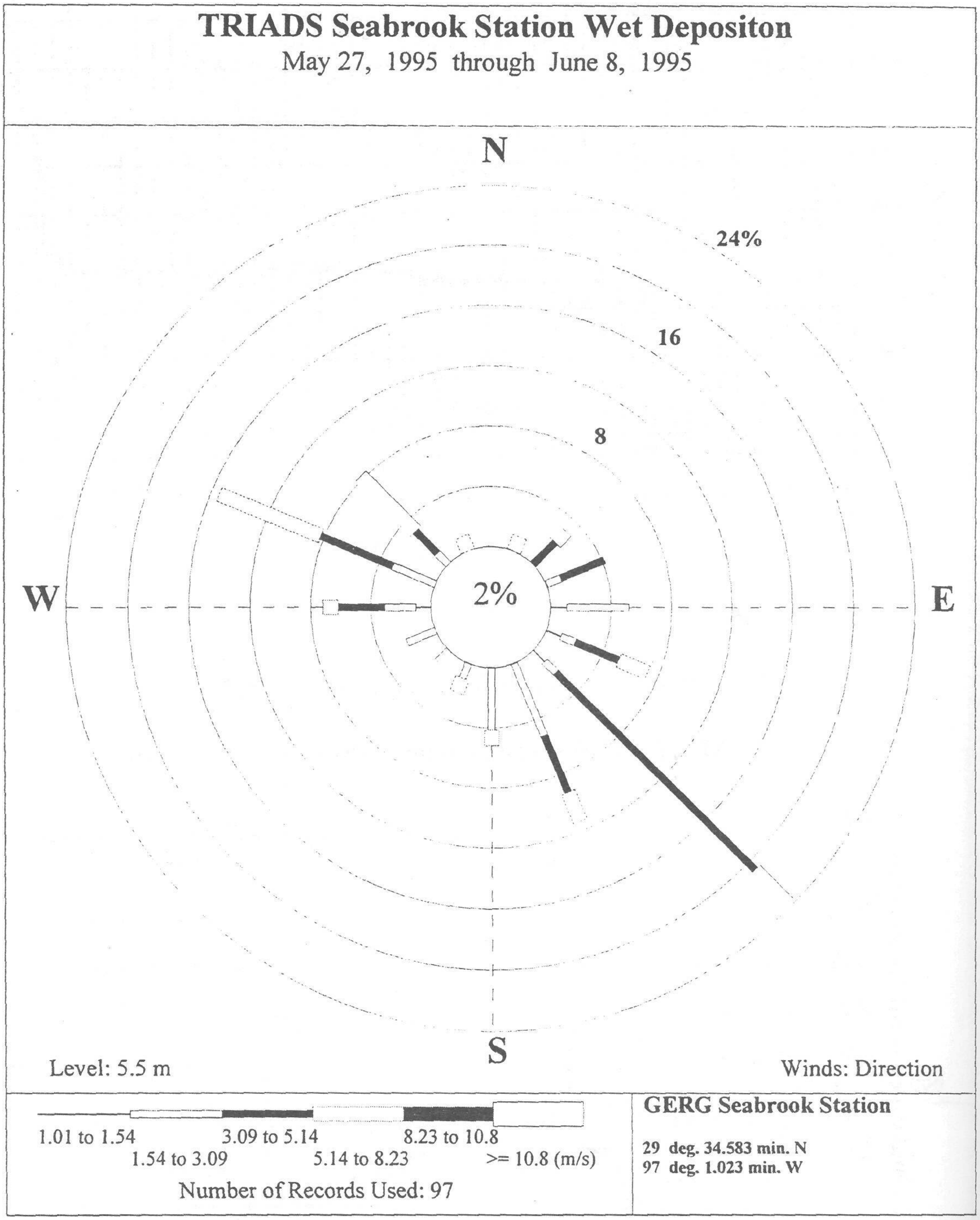


Figure 6. Wind Speed and Direction During May 27, 1995 through June 8, 1995 Rain Events.

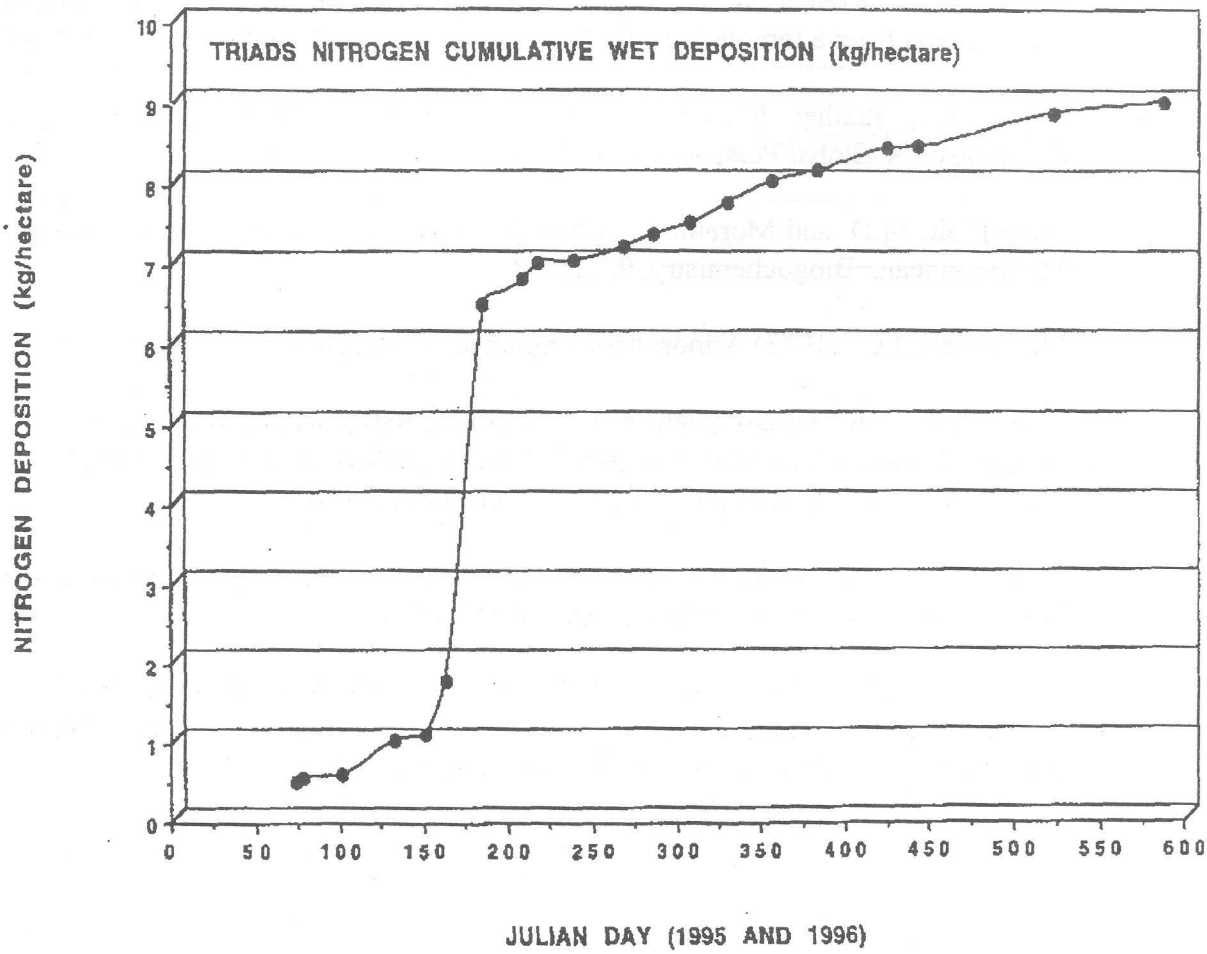


Figure 7. TRIADS Cumulative Wet Nitrogen Deposition (kg/hectare)

Bay. This percentage will likely increase as point sources directly to the water of nitrogen inputs are regulated.

Reference:

Gambell, A.W. and Fisher, D.W. (1964) Occurrence of sulfate and nitrate in rainfall, J. Geophys. Res., 69, 4203-10.

Healy, T.V., Mckay, H.A.C., Pilbeam, A., and Scargill, D. (1970) Ammonia and ammonium sulfate in the troposphere over the United Kingdom. J. Geophys. Res., 75, 2317-21.

Junge, C.E. (1963) Air Chemistry and Radioactivity. Academic Press, New York.

Likens, G.E., Kenne, W.C., Miller, J.M. and Galloway, J.N. (1987) Chemistry of precipitation from a remote terrestrial site in Australia. J. Geophys. Res., 92, 299-314.

Logan, J.A., Prather, M.J., Wofxy, S.C., and McElroy, M.B. (1981) Tropospheric Chemistry: A Global Perspective. J. Geophys. Res., 86. 7210-54.

Loye-Piolt, M.D. and Morelli, J. (1990) Atmospheric input of inorganic nitrogen to the Mediterranean. Biogochemistry, 9, 117-34.

McConnell, J.C. (1973) Atmospheric ammonia. J. Geophys. Res., 78, 7812-21.

Patwardhan, A.S. and Donigian, A.S., Jr., (1995) Assesment of nitrogen loads to aquatic system. National Exposure Research Laboratory, Office of Research and Development, U.S. EPA, Research Triangle Park, NC 27711. EPA/600/R-95/173.

Shon, Zangho (1994) Atmospheric input of nitrogen to the coastal region of southeastern Texas. MS thesis, Oceanograph, Texas A&M University.

Timperley, M.H., Vigoe-Brown, R.J., Kazwashima, M., and Ishigami, M. (1985) Organic nitrogen compounds in atmospheric precipitation: Their chemistry and availability to phytoplankton. Can. J. Fish. Aqua. Sci., 42, 401-14.